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A RIGID-BODY-BASED MULTIPLE TIME SCALE MOLECULAR DYNAMICS SIMULATION OF NANOPHASE MATERIALS

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Summary

Nanophase technology achieves superior material properties by assembling nanometer-size clusters. Structures on multiple-length scales and a hierarchy of time scales are essential for the design and control of nanophase materials. However, coexistence of a wide range of length and time scales hinders atomistic simulations of these materials. A new algorithm is developed for large-scale, longtime molecular dynamics simulations by combining (1) quaternion-based, rigid-body dynamics for global cluster motions; (2) implicit integration of Newton's equations for the coalescence of clusters; and (3) normal-mode analysis of fast atomic oscillations. The new scheme, using a time step Δt of 10^{-12} seconds, speeds up a conventional explicit integration scheme ($\Delta t = 2 \times 10^{-15}$ seconds) by a factor of 28. A parallel implementation of the scheme achieves an efficiency of 0.94 for a 1.28-million-atom nanocrystalline silicon nitride solid on 64 nodes of an IBM SP computer.

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Introduction

Nanophase technology is revolutionizing aerospace, surface transportation, electronics, and advanced manufacturing industries (Siegel, 1996). Superior material properties such as hardness and toughness are achieved by consolidating clusters of nanometer size (10^{-9} m) (see Figure 1).

Design of nanophase materials involves structures on multiple-length scales: atomic bonds (10^{-10} m); defects, micropores, and interfaces (10^{-9} m); and nanoclusters (10^{-8}-10^{-7} m) and their aggregates ($> 10^{-6}$ m). The essential issue is how atomic-level processes lead to superior materials properties on macroscopic scales. Since each cluster contains 10^4 to 10^5 atoms and material properties depend on the collective motion of 10^2 to 10^4 clusters, atomistic simulations involving 10^6 to 10^9 atoms are required. Recent developments in parallel processing technology and multiresolution numerical algorithms (Kalia et al., 1993; Nakano, Vashishta, and Kalia, 1993; Nakano, Kalia, and Vashishta, 1994; Nakano and Campbell, 1997) have enabled multimillion-atom simulations of nanophase materials based on the molecular dynamics (MD) method (Kalia, Nakano, Omeltchenko, et al., 1997; Kalia, Nakano, Tsuruta, et al., 1997; Tsuruta et al., 1998).

The multiple-length scale structures in nanophase materials lead to a hierarchy of time scales for their dynamics. For stable integration of the fastest atomic motions, the unit time step of MD simulations should be on the order of 10^{-15} seconds. However, rearrangement of nanoclusters takes place in 10^{-6} seconds or longer. The latter is essential for the control of various industrial processes such as gas phase condensation (Siegel, 1996) and sintering (Scherer, 1990). The challenge is to perform multimillion-atom MD simulations for the required 10^9 steps; such simulations are beyond the scope of current computational technology.

Large-scale simulations in diverse application areas are often associated with stiff dynamic systems (Hindmarsh and Petzold, 1995; Skeel, Zhang, and Schlick, 1997), which involve a wide range of time scales. An example is the conformational change of biomolecules (Zhang and Schlick, 1993). In quantum chemistry, stiff harmonic action arising from the kinetic energy of quantum particles (which is studied in quantum simulations with the unit time step of $\Delta t \sim 10^{-17}$ seconds) is inseparable from molecular motions on the time scale of 10^{-12} seconds (Tuckerman et al., 1996). In mineralogical simulations, stiff atomic motions in structural units (such as SiO_4 tetrahedra) are coupled to slow rearrangement of these units

(Hammonds et al., 1994). In astrophysics, billion-year evolution of the solar system is affected by planet motions on the time scale of a year (Wisdom and Holman, 1991). For further advancement of large-scale, longtime dynamic simulations, a multidisciplinary approach is needed.

Various approaches have been developed for longtime MD simulations. One approach introduces constraints to freeze high frequency modes. This enables the use of a large time step, assuming that the high-frequency modes are unimportant for global conformational changes (Ryckaert, Ciccotti, and Berendsen, 1977). In the subspace dynamics approach by Space, Rabitz, and Askar (1993), low-frequency modes are selected by diagonalizing the dynamical matrix of the system. Other schemes use different time steps for different force components (Streett, Tildesley, and Saville, 1978; Grubmüller et al., 1991; Tuckerman, Berne, and Martyna, 1991). Ordinary differential equations can be integrated using a large time step by implicit integration schemes (Hindmarsh and Petzold, 1995; Skeel, Zhang, and Schlick, 1997). For example, an implicit Euler integrator using time step Δt is a low-pass filter that selects motions with an eigenfrequency less than $1/\Delta t$; the frozen fast motions can be integrated separately by normal-mode analysis (Zhang and Schlick, 1993). Recently, more accurate implicit integrators have been proposed that are symplectic (Skeel, Zhang, and Schlick, 1997). Symplectic integrators preserve the phase-space volume, and this symplecticness is essential for longtime stability of orbitals (Arnold, 1989). It is also possible to take advantage of a special geometry of the system to significantly speed up longtime MD simulations. For example, an O(N) algorithm has been developed for the constraint dynamics of linear chain and tree geometry molecules (Jain, Vaidehi, and Rodriguez, 1993; Mathiowetz et al., 1994). In addition, proper coordinate transformations often separate the degrees of freedom with different time scales and thereby speed up numerical integration (Wisdom and Holman, 1991; Hammonds et al., 1994; Tuckerman et al., 1996).

In this paper, a new longtime integrator is developed for large-scale MD simulations of nanophase materials. The new algorithm combines (1) quaternion-based, rigid-body dynamics (Evans and Murad, 1977) for nanoclusters to represent their relative rotation; (2) implicit integration of Newton's equations (Skeel, Zhang, and Schlick, 1997) to represent the coalescence of clusters; and (3) normal-mode analysis of fast atomic oscillations (Zhang and Schlick, 1993). The rigid-body/implicit-integration/normal-mode (RIN) scheme is implemented

"The multiple-length scale structures in nanophase materials lead to a hierarchy of time scales for their dynamics."
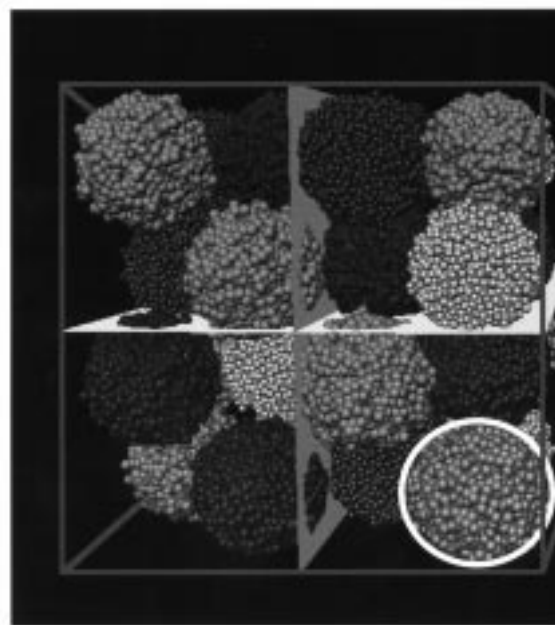

Fig. 1 Molecular dynamics simulations of nanocluster-assembled Si₃N₄ contain 108 clusters, each consisting of 10,052 atoms (total of 1,085,616 atoms). Small spheres represent Si or N atoms, and one of the nanoclusters is enclosed by a white circle. The walls represent partition boundaries to divide workloads used in the spatial decomposition scheme for parallel computing.

"The new algorithm combines (1) quaternion-based, rigid-body dynamics for nanoclusters to represent their relative rotation; (2) implicit integration of Newton's equations to represent the coalescence of clusters; and (3) normal-mode analysis of fast atomic oscillations."
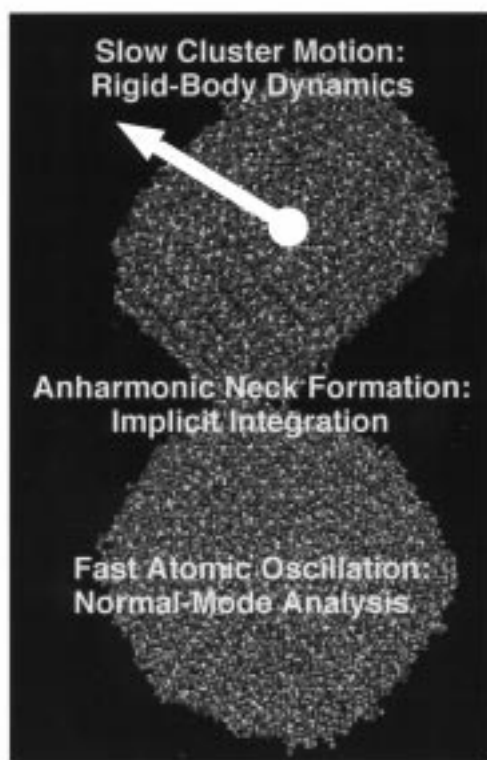
Fig. 2 Sintering of nanoclusters involves various physical processes that are treated efficiently with different numerical methods. (1) Rotation and translation of nanoclusters are included by rigid-body dynamics; (2) anharmonic atomic motions lead to the formation of a neck between clusters, and these motions are included by implicit integration of Newton's equations; and (3) thermal atomic motions assist the neck formation process, and these high-frequency modes are dealt with normal-mode analysis.

on parallel computers, and its performance is tested for million-atom nanophase materials.

Methods

Sintering is a process of densification by heating. This process is used to consolidate cluster-assembled nanophase materials. The early stage of sintering is driven by (1) the relative rotation of clusters (Tsuruta et al., 1996) and (2) the formation and growth of necks between clusters via surface diffusion or viscous flow (Scherer, 1990), while these processes are assisted by (3) local thermal motion of atoms (see Figure 2). Processes (1) and (2) are characterized by longtime scales ($> 10^{-9}$ seconds), compared with fast (10^{-13} seconds) atomic oscillations (3). A reliable longtime integrator of MD equations must at least capture these processes.

In MD simulations, a system is represented by a set of atomic coordinates, $\{\mathbf{x}_i \mid i = 1, \ldots, N\}$, where N is the number of atoms. Time evolution of the system is governed by Newton's equations (Allen and Tildesley, 1987),

$$m_i \frac{d^2 \mathbf{x}_i}{dt^2} = \mathbf{g}_i(\{\mathbf{x}_i\}), \tag{1}$$

where m_i and $\mathbf{g}_i(\{\mathbf{x}_i\}) = -\partial V/\partial \mathbf{x}_i$ are the mass and force for the ith atom, and $V(\{\mathbf{x}_i\})$ is the potential energy. We are concerned with systems for which the potential energy is a sum of an atomic pair and triple terms (Vashishta, Kalia, and Ebbsjö, 1995). The pair terms represent steric repulsion, electrostatic interaction due to charge transfer among atoms, and charge-dipole interaction. The triple terms represent covalent bond bending and stretching.

Given atomic coordinates $\mathbf{x}_i^n$ at time $t_n = n\Delta t$ ($n =$ integer), we integrate equation (1) for Δt using a reference system $\mathbf{r}_i$. The reference system is a tool designed to represent two of the essential dynamics (i.e., relative rotation of clusters and fast atomic oscillations). We thus define the reference system as a superposition, $\mathbf{r}_i = \mathbf{r}_{ci} + \mathbf{r}_{hi}$. The collective part $\mathbf{r}_{ci}$ represents the rigid-body motion of clusters, so that the system is represented by $6M$ degrees of freedom for the translational and rotational motion of M clusters ($M \ll N$). Equations of motion for the clusters are

$$M_c \frac{d^2 \mathbf{R}_c}{dt^2} = \mathbf{g}_c, \tag{2}$$

$$\frac{d\mathbf{L}_c}{dt} = \mathbf{T}_c, \tag{3}$$

where M_c, $\mathbf{R}_c$, and $\mathbf{L}_c$ are the mass, center of mass, and angular momentum of the cth cluster ($c = 1, \ldots, M$), respectively. In equations (2) and (3),

$$\mathbf{g}_c = \sum_{i \in c} \mathbf{g}_i^{\text{inter}}(\{\mathbf{r}_{ci}\}) \quad \text{and} \quad \mathbf{T}_c = \sum_{i \in c} m_i \mathbf{r}_{ci} \times \mathbf{g}_i^{\text{inter}}(\{\mathbf{r}_{ci}\})$$

are the force and torque on the cth cluster, where $\mathbf{g}_i^{\text{inter}}(\{\mathbf{r}_{ci}\}) = -\partial V_{\text{inter}} / \partial \mathbf{r}_{ci}$. The intercluster potential energy V_{inter} is the contribution from atomic pairs and triples whose elements belong to different clusters. Equations (2) and (3) are integrated for Δt using the quaternion formulation of rigid-body dynamics to avoid the numerical singularity associated with angular coordinates (Evans and Murad, 1977). The harmonic part $\mathbf{r}_{hi}$ represents the oscillation of each atom around the local potential minimum and is defined as a solution to the linear system,

$$m_i \frac{d^2 \mathbf{r}_{hi}}{dt^2} = -\mathbf{H}_{ii}(\mathbf{r}_{hi} - \mathbf{x}_i^*), \tag{4}$$

where $\mathbf{x}_i^*$ is the local potential minimum near $\mathbf{x}_i^n$ and the Hessian matrix,

$$\mathbf{H}_{ij} = \frac{\partial^2}{\partial \mathbf{x}_i \partial \mathbf{x}_j} V(\{\mathbf{x}_i\}), \tag{5}$$

is evaluated at $\mathbf{x}_i^*$. ($\mathbf{H}_{ij}$ is updated every time step.) The linear system, equation (4), describes independent harmonic motions of individual atoms, and it can be integrated analytically in terms of trigonometric functions (Zhang and Schlick, 1993).

The residual system $\mathbf{z}_i = \mathbf{x}_i - \mathbf{r}_i$ satisfies

$$m_i \frac{d^2 \mathbf{z}_i}{dt^2} = \mathbf{g}_i(\{\mathbf{z}_i + \mathbf{r}_i\}) - \mathbf{g}_i^{\text{inter}}(\{\mathbf{r}_{ci}\}) + \mathbf{H}_{ii}(\mathbf{r}_{hi} - \mathbf{x}_i^*). \tag{6}$$

The residual system is expected to vary slowly since the rapidly oscillating harmonic motions are subtracted. Therefore, equation (6) is integrated by an implicit integration scheme using Δt much larger than atomic time scales. One implicit integration scheme is equivalent to the conventional velocity Verlet algorithm (Allen and Tildesley, 1987), except that the force $\mathbf{g}_i^{n+1}$ at time ($n + 1)\Delta t$ is computed by solving a nonlinear equation (Skeel, Zhang, and Schlick, 1997),

$$\mathbf{g}_i^{n+1} = \mathbf{g}_i\left(\left\{\mathbf{x}_i^{n+1} + \frac{\Delta t^2}{2m_i}\mathbf{g}_i^{n+1}\right\}\right)$$
$$- \mathbf{g}_i^{\text{inter}}(\{\mathbf{r}_{ci}^{n+1}\}) + \mathbf{H}_{ii}(\mathbf{r}_{hi}^{n+1} - \mathbf{x}_i^*). \tag{7}$$

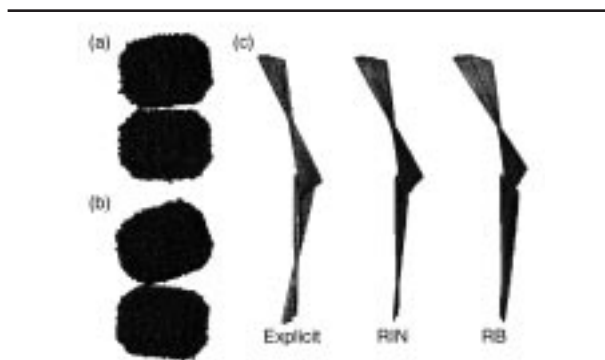*"The residual system is expected to vary slowly since the rapidly oscillating harmonic motions are subtracted."*

Fig. 3 (a) Starting molecular dynamics (MD) configuration of two 20,335-atom Si₃N₄ clusters. (b) The same system after 4×10^{-11} seconds. (c) Trace of the principal axes of the inertia tensors for the two Si₃N₄ clusters for 10^{-10} seconds. We compare explicit integration scheme with time step, $\Delta t = 2 \times 10^{-15}$ seconds (explicit); rigid-body (RB) dynamics using $\Delta t = 10^{-12}$ seconds; the rigid-body/implicit-integration/normal-mode (RIN) approach using $\Delta t = 10^{-12}$ seconds.

This implicit integration scheme is symplectic, and it is stable for an arbitrarily large Δt (Skeel, Zhang, and Schlick, 1997). Solving the nonlinear system, equation (7), is equivalent to the minimization of a dynamics function (Zhang and Schlick, 1993),

$$
\Phi(\{\mathbf{x_i}\}) = \sum_{i=1}^{N} \frac{m_i}{\Delta t^2}
$$

$$
\left[\mathbf{x}_i - \mathbf{x}_i^{n+1} + \frac{\Delta t^2}{2m_i} \left(\mathbf{g}_i(\{\mathbf{r}_{ci}^{n+1}\}) - \mathbf{H}_{ii}(\mathbf{r}_{hi}^{n+1} - \mathbf{x}_i^*) \right) \right]^2 \tag{8}
$$

$$
+ V(\{\mathbf{x_i}\}).
$$

In this variational formulation, equation (8) is minimized with respect to $\{\mathbf{x}_i\}$ by the truncated Newton method (Zhang and Schlick, 1993). After minimizing equation (8) at $\mathbf{x}_i^*$, the self-consistent force $\mathbf{g}_i^{n+1} = (2m_i / \Delta t^2)(\mathbf{x}_i^* - \mathbf{x}_i^{n+1})$ is used to accelerate the velocity of the residual coordinate, $\mathbf{z}_i$.

Numerical Results

Recently, million-atom parallel MD simulations have been performed to study the mechanical properties and fracture of nanophase Si₃N₄ (Kalia, Nakano, Omeltchenko, et al., 1997; Kalia, Nakano, Tsuruta, et al., 1997; Tsuruta et al., 1998). The simulations reveal self-affine behavior of fracture surfaces, which is very close to recent experimental observations (Daguier, Bouchaud, and Lapasset, 1995). The nanophase materials in these simulations were prepared by sintering hundreds of nanoclusters, and this procedure consumed much more computing time than the main fracture simulations. The purpose of this section is to examine whether the RIN scheme in the previous section can be used to prepare nanophase materials with significantly less computing time. To assess the validity of the RIN scheme in this context, we note the main findings of recent simulations on the sintering of Si₃N₄ nanoclusters (Tsuruta et al., 1996): (1) nanoclusters undergo significant rotational motion relative to each other, and (2) thermally rough nanoclusters form an asymmetric neck in 10^{-10} seconds. In the light of these findings, we test the validity of the RIN scheme in terms of cluster rotation and neck formation in 10^{-10} seconds.

The simulations involve two Si₃N₄ nanocrystals, each consisting of 20,335 atoms. The starting configuration is shown in Figure 3a. A reliable longtime integrator must first reproduce the longtime motion of clusters correctly. Rotational trajectories of a cluster may be visualized in terms of the inertia tensor,

$$I_{\alpha\beta} = \sum_i m_i \left(|\mathbf{d}_i|^2 \delta_{\alpha\beta} - \mathbf{d}_{i\alpha}\mathbf{d}_{i\beta} \right)(\alpha, \beta = x, y, z), \qquad (9)$$

where $\mathbf{d}_i$ is the coordinate of the ith atom relative to the cluster center of mass. An instantaneous configuration of a cluster is visualized by placing a line segment at the cluster center. The length and orientation of the line segment represent the largest eigenvalue and the corresponding eigenvector of $I_{\alpha\beta}$, respectively. Trajectory of the cluster is visualized as a trace of the line segment.

Figure 3c shows trajectories of the two clusters for 10^{-10} seconds. We compare three integration methods for Newton's equations: (1) explicit integration with the velocity Verlet scheme, using $\Delta t = 2 \times 10^{-15}$ seconds; (2) rigid-body (RB) cluster dynamics by freezing the other $3N - 6M$ degrees of freedom ($M = 2$); and (3) the RIN scheme. In both the RB and RIN schemes, we use $\Delta t = 10^{-12}$ seconds. Both of these schemes reproduce the trajectory of the explicit integration scheme accurately.

Sintering progresses through the formation of a "neck" between two clusters (see Figure 2). Figure 4 shows the time evolution of the neck size, which is defined as the number of atomic pairs whose elements belong to different clusters but are within a cutoff length (2 Å). The RIN scheme reproduces the explicit integration result satisfactorily, including the sudden increase of the neck size at 1.2×10^{-10} seconds. However, rigid-body dynamics alone cannot describe the neck formation. In fact, the two clusters bounce back and come apart in this scheme. (Note that the neck size in Figure 4 eventually becomes 0 with the RB scheme.)

Neck formation can also be monitored by the intercluster potential energy V_{inter}, as shown in Figure 5. The RIN scheme again reproduces the longtime behavior of V_{inter}, while the RB scheme fails to capture the lowering of V_{inter} by neck formation. In summary, the RIN scheme satisfactorily describes the essential longtime dynamics during sintering (i.e., relative cluster rotation and neck formation). Physically, the rigid-body reference system $\mathbf{r}_{ci}$ in the RIN scheme represents global cluster motions. As we have seen, however, the rigid-body dynamics cannot describe neck formation. Neck formation involves the breaking and formation of atomic bonds, and it cannot be described by the local harmonic analysis of equation (4) either. The implicit integration step in the RIN scheme takes this anharmonic effect into account. The importance of thermal atomic motions represented by $\mathbf{r}_{hi}$ is that they add random fluctuations to the initial configuration for the implicit integration step. In this way, they assist the neck formation, especially at high temperatures.
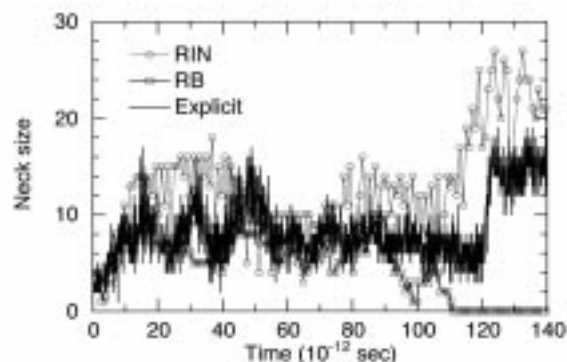

Fig. 4   Neck size between two Si$_3$N$_4$ clusters as a function of time. The circles and squares represent the results with the rigid-body/implicit-integration/normal-mode (RIN) and rigid-body (RB) schemes, respectively. They are compared with the result of the explicit integration scheme. The RB scheme fails to capture the neck formation between the two clusters, while the RIN scheme reproduces the explicit integration result satisfactorily.

"The RIN scheme satisfactorily describes the essential longtime dynamics during sintering (i.e., relative cluster rotation and neck formation)."
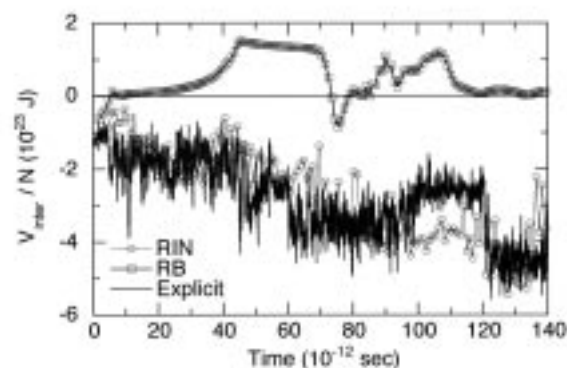

Fig. 5   Intercluster potential energy, V_{inter}, per atom as a function of time. The rigid-body/implicit-integration/normal-mode (RIN) scheme reproduces the explicit integration result correctly, while the rigid-body (RB) scheme fails to account for the lowering of V_{inter} by neck formation.
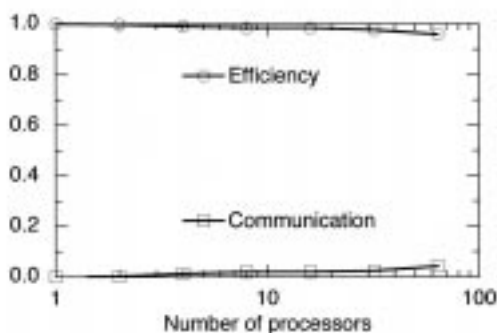
Fig. 6   Parallel efficiency and communication overhead of the parallel rigid-body/implicit-integration/normal-mode (RIN) program on the IBM SP computer at the Argonne National Laboratory. The system consists of α-Si$_3$N$_4$ nanoclusters, each containing 4,984 atoms. The number of atoms, *N*, scales with the number of processors, *p*, as *N* = 19,936 *p*.

Computation time of the RIN scheme to simulate the 40,670-atom Si$_3$N$_4$ system for 10^{-10} seconds is 5.4 hours on a single processor of Digital Alpha 2100/275. It takes 150 hours to simulate the same system using an explicit integration scheme. The RIN scheme thus speeds up a conventional MD integration scheme by a factor of 28. It is only possible by a low-cost computation scheme such as RIN to simulate multimillion-atom systems for technologically important time scales.

The RIN scheme is also implemented on distributed-memory parallel computers using spatial decomposition (Kalia et al., 1993; Nakano, Vashishta, and Kalia, 1993; Nakano, Kalia, and Vashishta, 1994; Nakano and Campbell, 1997). The entire system is divided into subdomains of the same volume according to uniform mesh decomposition, and each processor is assigned atoms in one subdomain (see Figure 1). To compute interatomic interaction, atomic information is exchanged across the partition boundaries by message passing.

The performance of the parallel RIN algorithm is tested on the 128-node IBM SP computer at Argonne National Laboratory. The simulated system is aggregates of Si$_3$N$_4$ clusters, each consisting of 4,984 atoms. We use the memory-bounded scaling so that the problem size is linearly proportional to the number of processors (Sun and Gustafson, 1991); each processor, on average, is assigned 19,936 atoms. The largest system contains 1,275,904 atoms on 64 processors. Figure 6 shows the parallel efficiency and communication overhead of the parallel RIN program on the SP machine. For the largest system, parallel efficiency $\eta = 0.94$, and communication overhead is 6% of the total computation time. One MD step ($\Delta t = 10^{-12}$ seconds) for the 1.28-million-atom system takes 7.5 minutes on 64 nodes of the SP computer. Argonne SP is a hybrid system consisting of IBM POWER processors of SP1 and the high-speed Omega switch of SP2 (Gropp and Lusk, 1994).

Conclusion

A new algorithm is developed for longtime MD simulations of cluster-assembled nanophase materials. The RIN algorithm combines (1) rigid-body cluster dynamics, (2) implicit integration of Newton's equations, and (3) normal-mode analysis. The new scheme, using a time step of 10^{-12} seconds, speeds up the conventional explicit integration scheme, using a time step of 2×10^{-15} seconds, by a factor of 28. The RIN scheme accurately describes the essential features of nanocluster sintering (i.e., cluster

rotation and neck formation). A parallel implementation of the scheme achieves an efficiency of 0.94 for a 1.28-million-atom Si_3N_4 nanocrystalline solid on 64 nodes of an IBM SP computer. More recently, fuzzy clustering has been shown to further improve the accuracy of the RIN scheme (Nakano, 1997). For efficient preparation of nanophase materials, we are also exploring the use of a hybrid scheme that combines the grand canonical Monte Carlo method (Mezei, 1980) and the RIN-based MD.

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BIOGRAPHY

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